Electronic Supplementary Information for Dalton Transactions

Synthesis, characterisation and coordination chemistry of a new multidentate P_2N_4 ligand system

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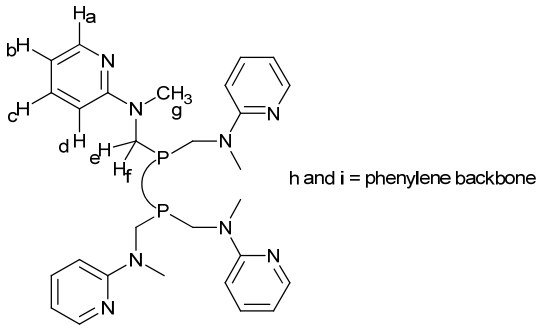
Supplementary information

Table 1: Summary of $^{31}P\{^1H\}$ and ^1H NMR chemical shift data for **1**, **2**, **3** and **4**.

	$^{31}P\{^1H\}$ NMR (ppm)	^1H NMR (ppm)								
		a	b	c	d	e	f	g	h	i
P_2N_4 (**1**)	-38.5	8.05	6.47	7.32	6.44	4.46	4.12	2.91	7.80-7.72	7.45-7.38
$[PdCl_2(P_2N_4)]$ (**2**)	65.9	7.83	6.48	7.37-7.32	6.38	5.35	4.46	3.00	7.37-7.32	7.20-7.18
$[PtCl_2(P_2N_4)]$ (**3**)	40.3	7.82-7.80	6.46	7.34-7.29	6.33	5.34	4.41	3.04	7.91-7.89	7.15-7.13
$[Pt(P_2N_4)](ClO_4)_2$ (**4**)	36.3	8.13	7.04	7.83-7.79	6.99-6.96	4.73	4.41	2.97	8.28-8.25	7.87-7.86



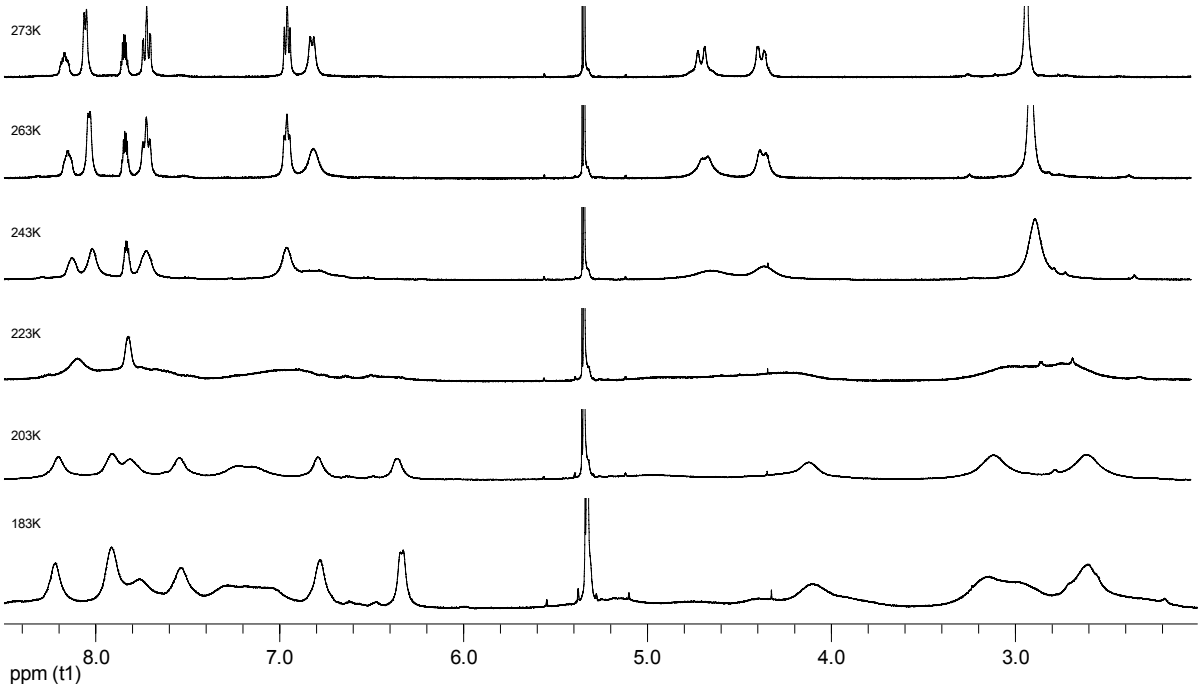


Fig. 1 Variable temperature ^{1}H NMR spectra of complex **4** in CD_2Cl_2.

Experimental

General considerations

All preparations were carried out using standard Schlenk line techniques under an inert atmosphere of N_2 unless otherwise stated. Solvents were dried over standard drying agents and freshly distilled under nitrogen before use. All starting materials were of reagent grade, purchased from either Aldrich Chemical Company or Strem Chemicals. Chromatographic separations were carried out on Kieselgel 60 SiO_2. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded on Bruker Av-400, DRX-400, Av-500 spectrometers. Chemical shifts are reported in ppm using the residual proton impurities in the solvents. Pseudo-triplets which occur as a result of identical J-value coupling to two chemically inequivalent protons are assigned as dd and are recognised by the inclusion of only one J-value. Positive-ion FAB and electron ionisation mass spectra were recorded on a Micromass Autospec Q spectrometer using a 3-nitrobenzyl alcohol matrix. Electron ionisation was carried out at 70 eV. Infrared

spectra were recorded on a Perkin-Elmer 983G spectrophotometer equipped with a Perkin-Elmer 3700 data station and recorded as a solution in dichloromethane. Elemental analyses were carried out by Mr. Stephen Boyer of the Department of Health and Human Sciences, London Metropolitan University. X-ray diffraction analysis was carried out by Dr. Andrew White of the Department of Chemistry at Imperial College London.

P_2N_4 (1)

To a solution of 1,2-bis[bis(hydroxymethyl)phosphino]benzene (1.00 g, 3.81 mmol) in dry degassed methanol (25 ml) was added 2-methyl-aminopyridine (1.57 ml, 15.2 mmol) and the mixture brought to reflux for 24 hrs. After this time, methanol was removed *in vacuo* to yield a thick viscous colourless liquid in quantitative yield based on the $^{31}P\{^{1}H\}$ NMR spectrum of the mixture. An analytically pure sample could be obtained following purification by column chromatography using silica gel as the stationary phase and diethyl ether as the eluent. Anal. Calc. for $C_{34}H_{40}N_8P_2$: C, 65.58; H, 6.47; N, 18.00. Found: C, 65.45; H, 6.42; N, 17.90. IR (ν/cm^{-1}) CH_2Cl_2: 1597 (Py), 1560, 1493, 1422, 1377, 1319, 1272, 1266, 1265, 1256, 1230, 1205, 1161, 985, 896, 863. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05 (dd, 4H, $^{3}J_{HH}$ = 4.9 Hz, $^{4}J_{HH}$ = 1.3 Hz,), 7.80-7.72 (m, 2H,), 7.45-7.38 (m, 2H), 7.32 (ddd, 4H, $^{3}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 7.2 Hz $^{4}J_{HH}$ = 1.9 Hz), 6.47 (dd, 4H, $^{3}J_{HH}$ = 7.0 Hz, $^{3}J_{HH}$ = 5.1 Hz), 6.44 (d, 4H, $^{3}J_{HH}$ = 8.6 Hz), 4.46 (d, 4H, $^{2}J_{HH}$ = 14.4 Hz), 4.12 (d, 4H, $^{2}J_{HH}$ = 14.4 Hz), 2.91 (s, 12H). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz): δ -38.5. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 158.4 (s, Ar *C*), 147.6 (s, Ar *C*H), 137.5 (d, $^{1}J_{PC}$ = 36.8 Hz, Ar *C*), 137.0 (s, Ar *C*), 132.0 (s, Ar *C*H), 129.3 (s, Ar *C*H), 111.6 (s, Ar *C*H), 106.3 (s, Ar *C*H), 50.3 (s, *C*H_2), 37.0 (s, *C*H_3). Electrospray TOF-MS: m/z (%): 623 (100) [$C_{34}H_{40}N_8P_2^{+}$].

[$PdCl_2(P_2N_4)$] (2)

To a solution of $N_2P_2N_{2\{phen\}}$ (0.075g, 0.12 mmol) in dichloromethane (10 mL) was added [$PdCl_2$(COD)] (0.034g, 0.12 mmol) and the mixture allowed to stir for two hours at ambient temperature. The complex was isolated as an orange powder following precipitation of the dichloromethane solution with excess pentane (yield = 89%). Crystals suitable for X-ray diffraction were obtained by slow evaporation of a chloroform solution from an NMR tube over a period of 5 days. Anal. Calc. for $C_{34}H_{40}Cl_2N_8P_2Pd$: C, 51.04; H, 5.04; N, 14.01. Found: C, 51.07; H, 4.99; N, 13.96. IR (ν/cm^{-1}) CH_2Cl_2: 1595 (Py), 1563, 1490, 1426, 1370, 1320, 1279, 1265, 1259, 1239, 1160, 990, 865. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83 (dd, 4H, $^3J_{HH}$ = 4.8 Hz, $^4J_{HH}$ = 1.4 Hz), 7.37-7.32 (m, 2H), 7.20-7.18 (m, 2H), 6.48 (dd, 4H, $^3J_{HH}$ = 7.0 Hz, $^3J_{HH}$ = 5.1 Hz), 6.38 (d, 4H, $^3J_{HH}$ = 8.5 Hz), 5.35 (d, 4H, $^2J_{HH}$ = 14.8 Hz), 4.46 (d, 4H, $^2J_{HH}$ = 14.8 Hz,), 3.00 (s, 12H). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 65.9. FAB-MS: m/z (%): 765 (40) [$C_{34}H_{40}ClN_8P_2Pd^+$].

[$PtCl_2(P_2N_4)$] (3)

Complex **3** was prepared using [$PtCl_2$(COD)] in a method analogous to that previously described for **2**. Crystals of **3** were obtained by slow diffusion of diethyl ether into a dichloromethane solution (yield = 65%). Anal. Calc. for $C_{34}H_{40}Cl_2N_8P_2Pt$: C, 45.95; H, 4.54; N, 12.61. Found: C, 46.03; H, 4.48; N, 12.69. IR (ν/cm^{-1}) CH_2Cl_2: 1595 (Py), 1563, 1491, 1426, 1372, 1320, 1274, 1270, 1266, 1262, 1256, 1160, 990, 867. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91-7.89 (m, 2H), 7.82-7.80 (m, 4H), 7.34-7.29 (m, 4H), 7.15-7.13 (m, 2H), 6.46 (dd, 4H, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 5.2 Hz), 6.33 (d, 4H, $^3J_{HH}$ = 8.5 Hz), 5.34 (dd, 4H, $^2J_{HH}$ = 14.9 Hz, $^2J_{PH}$ = 3.52 Hz) with Pt satellites, ($^3J_{Pt\text{-}H}$ = 58 Hz), 4.41 (dd, 4H, $^2J_{HH}$ = 14.9 Hz, $^2J_{PH}$ =

2.2 Hz), 3.04 (s, 12H). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz): δ 40.3 with Pt satellites, ($^{1}J_{Pt\text{-}P}$ = 3440 Hz). TOF MS ES+: m/z (%): 870 (30), 843 (100), 750 (80).

$[Pt(P_2N_4)](ClO_4)_2$ (4)

To complex **3** (50 mg, 0.056 mmol) in dichloromethane (5 mL) was added $AgClO_4$ (23 mg, 0.112 mmol) and the mixture allowed to stir at ambient temperature in darkness overnight. The reaction mixture was then filtered through a pad of celite filter aid and evaporated to dryness (yield = 95 %). Crystals suitable for single crystal X-ray diffraction studies were obtained by slow evaporation of an acetone solution the complex over a period of 3 days. Anal. Calc. for $C_{34}H_{40}Cl_2N_8O_8P_2Pt$: C, 40.17; H, 3.97; N, 11.02. Found: C, 40.09; H, 3.97; N, 10.94. IR (ν/cm^{-1}) CH_2Cl_2: 1596 (Py), 1564, 1490, 1427, 1370, 1322, 1274, 1269, 1262, 1256, 1160, 1097 (ClO_4), 992, 954, 896. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.28-8.25 (m, 2H), 8.13 (d, $^{3}J_{HH}$ = 5.3 Hz), 7.97-7.96 (m, 2H), 7.83-7.79 (m, 4H), 7.04 (d, 4H, $^{3}J_{HH}$ = 8.4 Hz), 6.99-6.96 (m, 4H), 4.73 (dd, 4H, $^{2}J_{HH}$ = 14.8 Hz, $^{2}J_{PH}$ = 3.33 Hz) with Pt satellites, ($^{3}J_{Pt\text{-}H}$ = 49 Hz), 4.41 (dd, 4H, $^{2}J_{HH}$ = 14.8 Hz, $^{2}J_{PH}$ = 2.0 Hz), 2.97 (s, 12H). $^{31}P\{^{1}H\}$ NMR CD_2Cl_2, 162 MHz): δ 36.3 with Pt satellites, ($^{1}J_{Pt\text{-}P}$ = 3227 Hz). TOF MS ES+: m/z (%): 870 (40), 843 (95), 750 (100).

Supporting Information — X-Ray Crystallography

Crystal data for **2**: $C_{34}H_{40}Cl_2N_8P_2Pd{\cdot}CH_2Cl_2$, M = 884.91, monoclinic, $P2_1$ (no. 4), a = 8.76972(13), b = 20.6503(3), c = 11.06358(17) Å, β = 96.2403(14)°, V = 1991.72(6) Å^3, Z = 2, D_c = 1.476 g cm^{-3}, μ(Mo-Kα) = 0.851 mm^{-1}, T = 173 K, pale yellow blocky needles, Oxford Diffraction Xcalibur 3 diffractometer; 12040 independent measured reflections (R_{int} = 0.036), F^2 refinement, R_1(obs) = 0.028, wR_2(all) = 0.071, 11728 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 65°], 499 parameters. The absolute structure of **4** was unambiguously determined by a combination of R-factor tests [R_1^+ = 0.0281, R_1^- = 0.0329] and by use of the Flack parameter [x^+ = +0.071(14), x^- = +0.929(14)]. CCDC 724551.

Crystal data for **3**: $C_{34}H_{40}Cl_2N_8P_2Pt$, M = 888.67, triclinic, $P\bar{1}$ (no. 2), a = 8.72951(16), b = 11.3275(3), c = 19.0652(4) Å, α = 82.7178(19), β = 88.0625(16), γ = 71.5368(19)°, V = 1773.73(7) Å^3, Z = 2, D_c = 1.664 g cm^{-3}, μ(Cu-Kα) = 9.935 mm^{-1}, T = 173 K, colourless needles, Oxford Diffraction Xcalibur PX Ultra diffractometer; 6780 independent measured reflections (R_{int} = 0.022), F^2 refinement, R_1(obs) = 0.019, wR_2(all) = 0.048, 6275 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 143°], 429 parameters. CCDC 724552.

Crystal data for **4**: $[C_{34}H_{40}N_8P_2Pt](ClO_4)_2{\cdot}Me_2CO$, M = 1074.75, monoclinic, $P2_1/c$ (no. 14), a = 18.35407(18), b = 16.07748(18), c = 14.12043(14) Å, β = 90.4399(8)°, V = 4166.64(7) Å^3, Z = 4, D_c = 1.713 g cm^{-3}, μ(Mo-Kα) = 3.636 mm^{-1}, T = 173 K, colourless blocks, Oxford Diffraction Xcalibur 3 diffractometer; 13229 independent measured reflections (R_{int} = 0.028), F^2 refinement, R_1(obs) = 0.031, wR_2(all) = 0.080, 11448 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max}$ = 65°], 590 parameters. CCDC 724553.

The positions of the nitrogen atoms of the non-coordinated pyridine moieties in the structures of **2**, **3** and **4** were determined by (a) comparison of thermal parameters when both possible sites were refined as carbon atoms, (b) locating the C–H protons from ΔF maps, and (c) inspection of the bond lengths. This assignment process was complicated in the case of the structure of **2** by the presence of disorder for two of ligand arms (*vide infra*), Additionally, none of the four *ortho* C–H protons could be located. Despite these problems, however, the pyridyl nitrogen atoms were clearly located based on their lower thermal parameters when handled as carbon. It was also noted that in the two previously determined structures containing this ligand (**3** and **4**, neither of which showed any disorder in the ligand) the pyridyl nitrogen atom has always adopted a position *anti* to the proximal nitrogen bound methyl group. The N(24) and N(44) pyridyl rings were both found to be disordered, and in each case two partial occupancy orientations were identified [*ca.* 73:27 and 71:29 for the N(24) and N(44) rings respectively] and only the non-hydrogen atoms of the major occupancy orientations were refined anisotropically. The included dichloromethane solvent was also found to be disordered. Three orientations of *ca.* 49, 38 and 13% occupancy were identified, and only the chlorine atoms were refined anisotropically. The compound crystallised in a chiral space group, and the absolute structure was unambiguously determined by a combination of *R*-factor tests [$R_1^+ = 0.0281$, $R_1^- = 0.0329$] and by use of the Flack parameter [$x^+ = +0.071(14)$, $x^- = +0.929(14)$]. In the structure of **4**, disorder was found in one of the perchlorate anions and the included acetone solvent molecule. For the perchlorate anion, three partial occupancy orientations were identified of *ca.* 40, 32 and 28% occupancy, and only the central chlorine atom of each orientation was refined anisotropically. For the acetone solvent molecule, two partial occupancy orientations were identified of *ca.* 80 and 20% occupancy, and only the non-hydrogen atoms of the major occupancy orientation were

refined anisotropically. Of the nine largest residual electron density peaks, only the top one is not proximal to the platinum atom. This peak, of *ca.* 1.98 eÅ^{-3}, was assigned as a crystallographic artefact for two reasons. Firstly, it is located in a chemical implausible position, being sited *ca.* 1.65 Å away from an oxygen atom of the ordered perchlorate anion [O(13)], and *ca.* 1.44 Å from the aromatic proton on C(5). Secondly, refinement of the data from an earlier rapid data collection on the same crystal (*ca.* 4 hours, *cf. ca.* 67 hours for the data reported here) also had this artefact present, but much larger at *ca.* 4.4 eÅ^{-3}. That a higher quality data collection leads to significant shrinkage of the magnitude of this rogue peak strongly argues for it not being real.

Tables

Table S1. Selected bond lengths (Å) and angles (°) for **2**.

Pd–Cl(1)	2.3692(5)	Pd–Cl(2)	2.3700(6)
Pd–P(1)	2.2184(5)	Pd–P(2)	2.2154(5)
Cl(1)–Pd–Cl(2)	95.80(2)	Cl(1)–Pd–P(1)	173.16(2)
Cl(1)–Pd–P(2)	86.801(19)	Cl(2)–Pd–P(1)	90.90(2)
Cl(2)–Pd–P(2)	176.66(2)	P(1)–Pd–P(2)	86.46(2)

Table S2. Selected bond lengths (Å) and angles (°) for **3**.

Pt–Cl(1)	2.3584(6)	Pt–Cl(2)	2.3616(6)
Pt–P(1)	2.2043(7)	Pt–P(2)	2.2069(6)
Cl(1)–Pt–Cl(2)	92.59(2)	Cl(1)–Pt–P(1)	174.40(2)
Cl(1)–Pt–P(2)	87.26(2)	Cl(2)–Pt–P(1)	92.01(2)
Cl(2)–Pt–P(2)	179.59(3)	P(1)–Pt–P(2)	88.16(2)

Table S3. Selected bond lengths (Å) and angles (°) for **4**.

Pt–P(1)	2.1879(7)	Pt–P(2)	2.1880(8)
Pt–N(14)	2.119(3)	Pt–N(34)	2.131(2)
P(1)–Pt–P(2)	88.24(3)	P(1)–Pt–N(14)	85.58(7)
P(1)–Pt–N(34)	167.91(8)	P(2)–Pt–N(14)	173.66(7)

P(2)–Pt–N(34)	86.84(7)	N(14)–Pt–N(34)	98.95(10)

Figure Captions

Fig. S1 The molecular structure of **2** (50% probability ellipsoids).

Fig. S2 The molecular structure of **3** (50% probability ellipsoids).

Fig. S3 The molecular structure of **4** (50% probability ellipsoids).

Figures

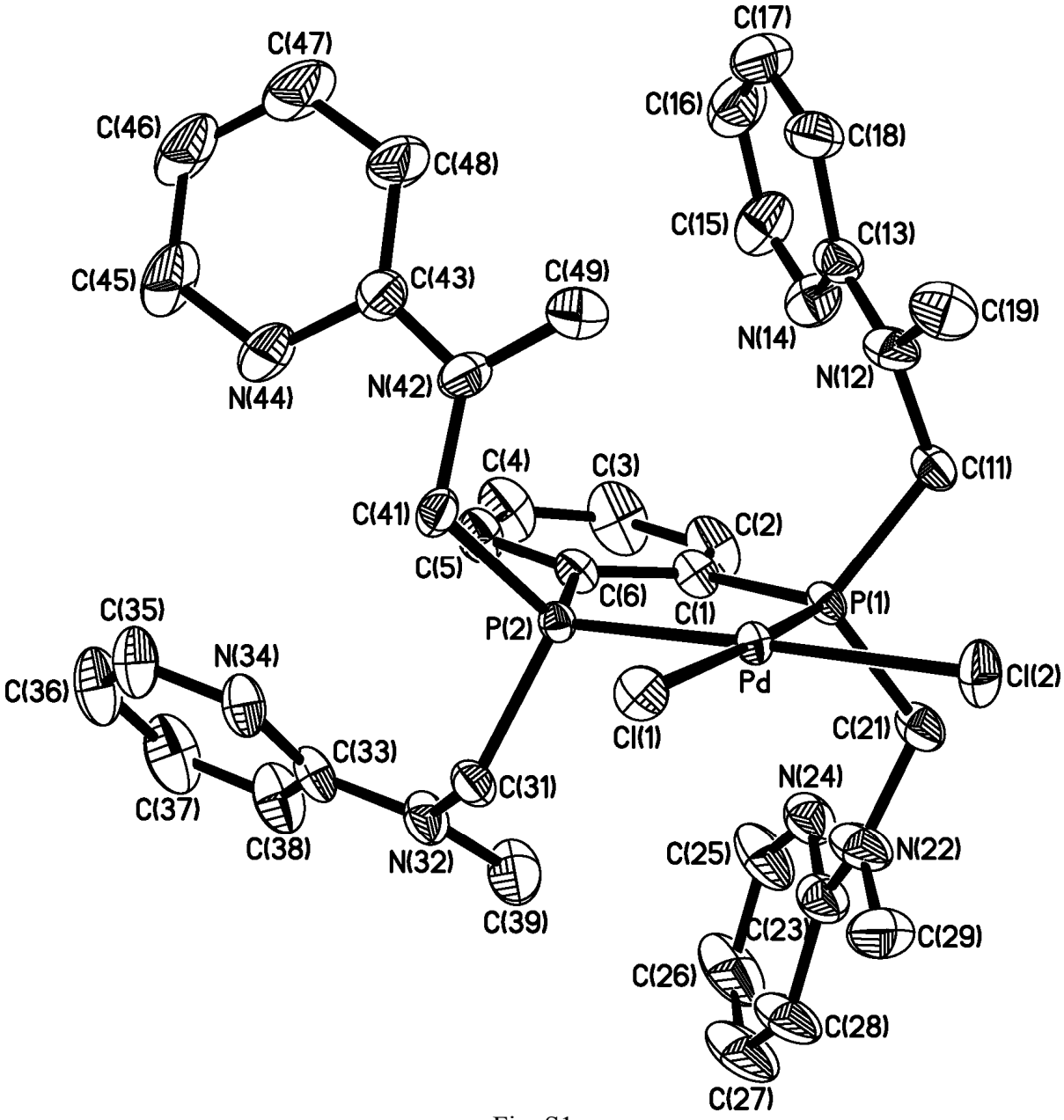
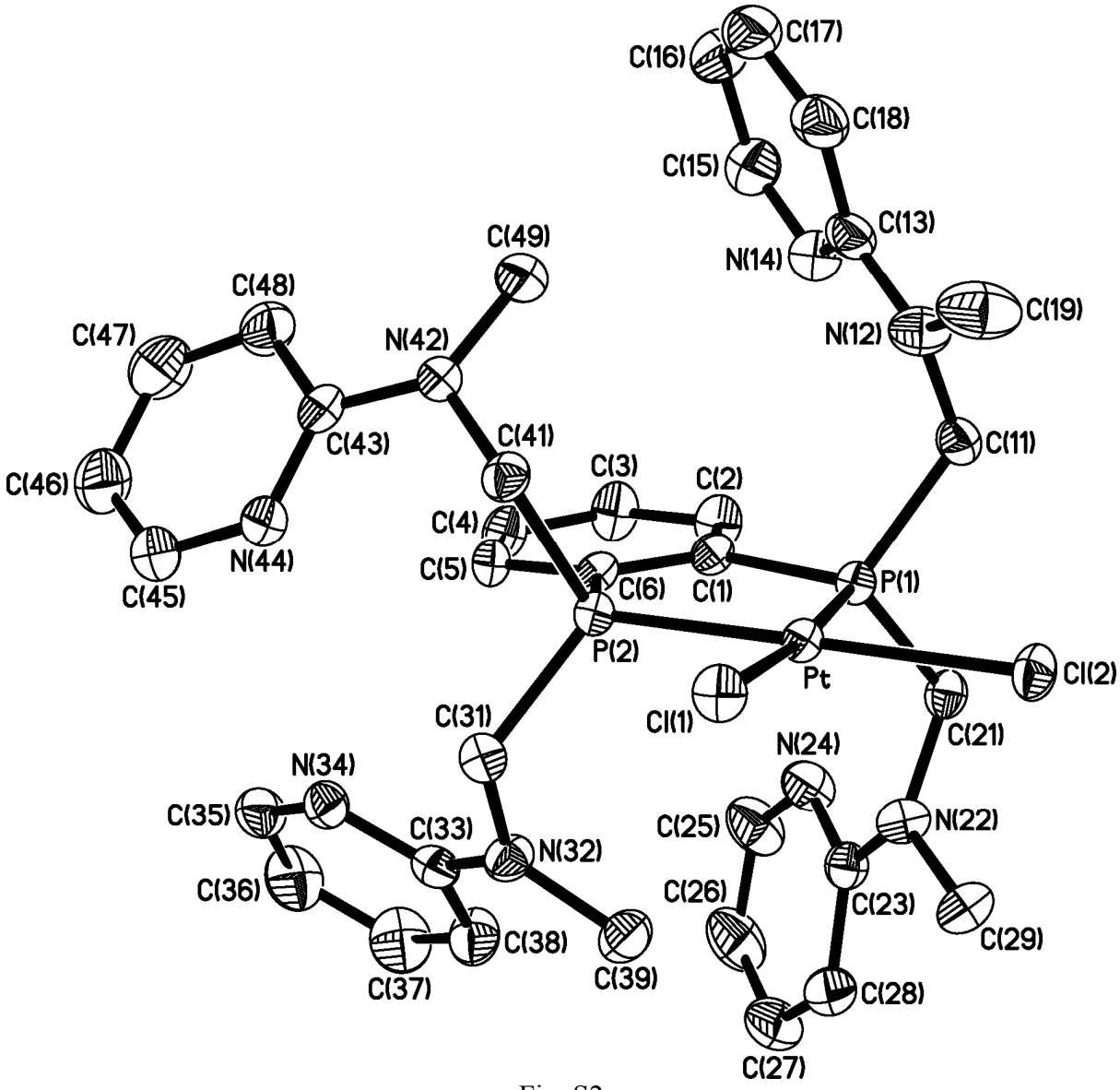


Fig. S1



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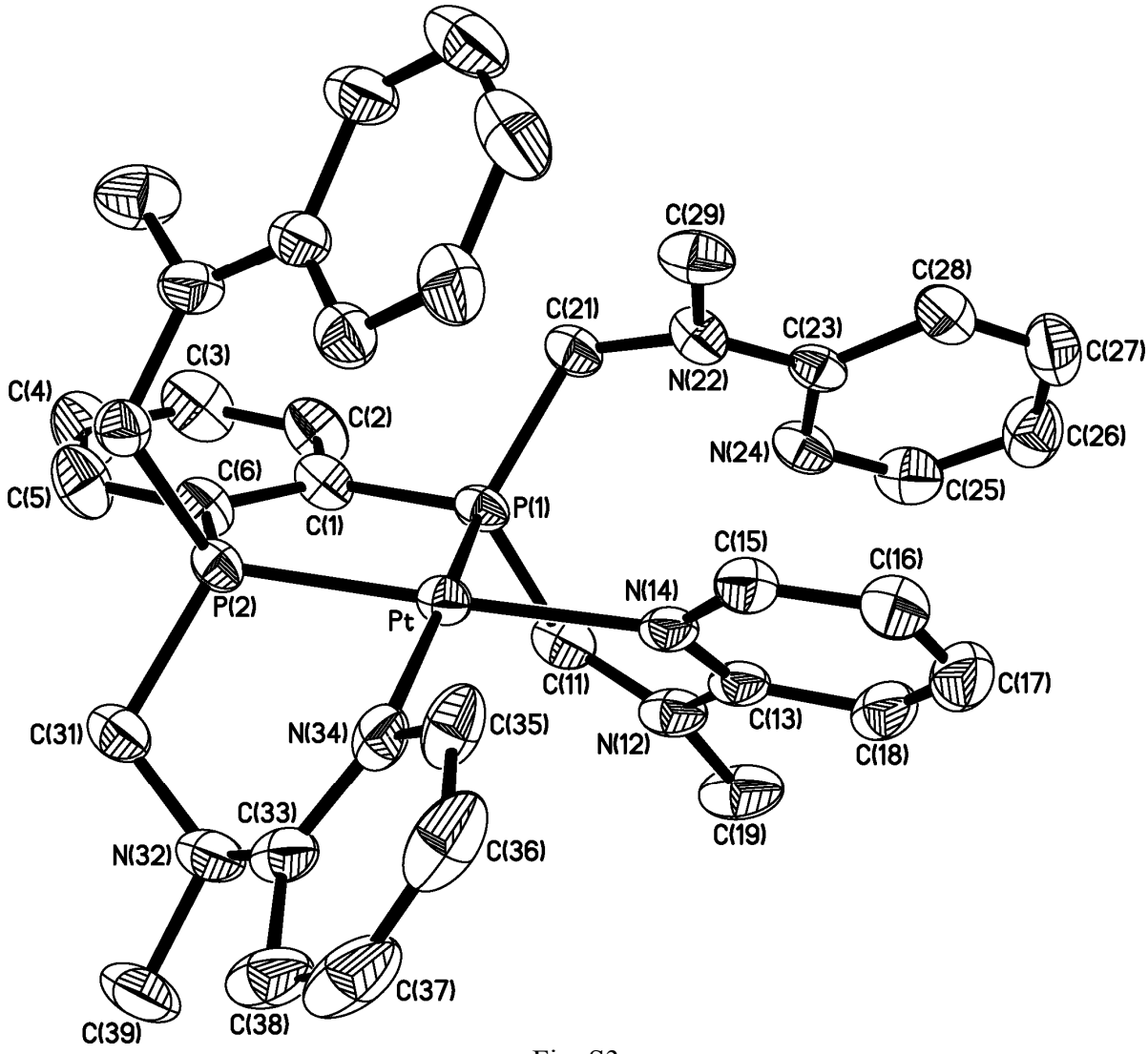

Fig. S3